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(54) Heat treatment of Si single crystal

Wärmebehandlung von Silizium-Einkristall

Traitement thermique de silicium monocristallin

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Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to heat treatment of a Si single crystal. More particularly, this invention relates to heat treatment of a Si single crystal for production of a Si wafer excellent in oxide film dielectric breakdown voltage characteristic.

DESCRIPTION OF THE PRIOR ART

Increasingly high integration of semiconductor circuits and the attendant miniaturization of their elements have been urging a growing decrease in thickness of insulating oxide films in the gate electrode parts of MOS-LSI. Even these thin insulating oxide films are required to exhibit a high dielectric breakdown voltage during the operation of relevant device elements, suffer only a small leak current, and fulfil their functions with high reliability.

For the production of these device elements, Si single crystals produced by the Czochralski method are used. The Si single crystals of the Czochralski method contain crystal defects owing to the thermal history experienced in highly heated portions during the growth of crystal.

When LSI elements are formed with a wafer from a Si single crystal containing such crystal defects, the insulating oxide films in the elements offer a problem of inferior dielectric breakdown voltage.

For a given Si wafer to allow production of LSI elements in a high yield, it is important that the Si wafer should be free from such defects as to impair the dielectric breakdown voltage characteristic of the oxide film.

These crystal defects are found to be correlated with the speed of growth of a crystal; the density of defects decreases and consequently the dielectric breakdown voltage characteristic of an oxide film improves in accordance as the speed of crystal growth decreases. From the commercial point of view, the Si single crystals produced with due respect to this correction have a problem of poor efficiency on account of a low speed of crystal growth.

This problem will be discussed below on the basis of the knowledge the inventors acquired during their study which led to perfection of this invention. Fig. 4 shows the density of defects in a wafer taken from a Si single crystal produced by the conventional technique in relation to the speed of crystal growth. The determination of the density of defects was carried out by etching a given wafer for 30 minutes in accordance with the selective etching method (the method using an etching solution consisting of 2 g of $K_2Cr_2O_7$, 50 ml of H_2O, and 100 ml of HF; Secco D'Arragona, F.: J. Electrochem. Soc., 119: 948, 1972) and then taking count of scale-like patterns formed on the etched surface as observed under an optical microscope. The density of scale-like patterns was 20 counts/cm^2 when the speed of crystal growth was as low as 0.4 mm/min. When the speed of crystal growth exceeded 1 mm/min., however, this density was as high as 1,000/cm^2.

Wafers of this class were tested for determination of the dielectric breakdown voltage characteristic of oxide film. The determination of the dielectric breakdown voltage characteristic of oxide film was carried out by forming 100 elements in a given Si wafer, selecting out as acceptable products the elements whose oxide films had dielectric breakdown voltages exceeding 8 MV/cm. For testing the oxide film dielectric breakdown voltage characteristic, gate parts measuring 8 mm^2 in area and made of polysilicon were used. The formation of an oxide film were carried out at 900°C for 100 minutes (in an atmosphere of dry oxygen). The oxide films had a thickness of 250Å .

The actual results of determination are illustrated in terms of relation between the ratio of acceptable products (with sufficiently high oxide film dielectric breakdown voltage) and the density of scale-like patterns. In the case of a Si wafer which registered a high density of scale-like patterns of 1,000 counts/cm^2, the ratio of acceptable products because of sufficiently high oxide film dielectric breakdown voltage was about 40%. When the density of scale-like patterns was about 200 counts/cm^2, the ratio of acceptable products was 80%. These results indicate that the improvement of the ratio of acceptable products of sufficiently high oxide film dielectric breakdown voltage requires to decrease the density of scale-like patterns appearing during the selective etching, namely to decrease the density of defects.

SUMMARY OF THE INVENTION

This invention, conceived in the urge to overcome the drawbacks of the prior art mentioned above aims to provide a method which, in a wafer from a Si single crystal, effects elimination of crystal defects possibly contained while the Si single crystal is grown at the lowest costwise acceptable speed.

In accordance with the present invention there is provided a method for heat treatment of a wafer cut out of a Si single crystal bar grown by the Czochralski method at a speed of pull exceeding 0.8 mm/min. and not higher than 1.6 mm/min. at a temperature in the range 1150°C to 1280°C for the purpose of obtaining a Si single crystal wafer with an improved oxide film dielectric breakdown voltage; characterised by:

determining, in advance, a first correlation between the oxide film breakdown voltage and the density of scale-like patterns as obtained by selective etching of the wafer, and a second correlation between said density of scale-like patterns and the time period of

the heat treatment; and

heat treating the Si single crystal wafer within said temperature range in an atmosphere of dry oxygen for a time period of at least 10 minutes, selected on the basis of said first and second correlations such that the Si single crystal wafer has a density of scale-like patterns not higher than 200 counts/cm^2 after the heat treatment, which is required to improve the oxide film dielectric breakdown voltage to not less than 8MV/cm.

EP-A-0390672 discloses a technique for regulating the precipitated interstitial oxygen by thermal treatment at 400°C to 500°C in an atmosphere of dry oxygen. Higher temperature processing at 1280°C in an atmosphere of dry oxygen is performed as a preliminary step for the purpose of initializing the heat history during crystal growing. The particular object of this technique is to obtain uniform oxygen precipitation in the crystal growth direction (page 2, lines 34 to 36).

JP-A-57-200293 (Patent Abstracts of Japan, Vol. 7, No. 46 (C-153)[1191], 23.02.1983) discloses heat treatment at 1150°C to 1250°C in a non-oxidizing atmosphere for 2 hours or longer, as the second step of a three-part heat treatment. The temperatures employed in this treatment are selected for the purposes of an intrinsic gettering (IG) process of silicon single crystals. The thermal treatment described requires a first step at 600°C to 800°C for ten hours or longer in dry oxygen, nitrogen or argon, a second step at 1150°C to 1250°C for two hours or longer in a non-oxidizing atmosphere, and a third step at 950°C to 1050°C for one hour or longer in an oxidizing atmosphere.

GB-A-2080780 discloses heat treatment for diffusing out interstitial oxygen as the first step of a two step heat treatment. This two step process involves a first step at a temperature above 1100°C (1150°C to 1350°C) for 2 to 24 hours sufficient for oxygen to diffuse from the surface region, and a second step at a temperature of 550°C to 950°C for a time sufficient to nucleate defects, prior to cooling the wafer slice below 300°C.

J. Electrochem. Soc. 119(2), 02.02.1972, pp. 255-265, D.I. Pomerantz: "Effects of Grown-in and Process-Induced Defects in Single Crystal Silicon" discloses thermal treatment carried out for the purpose of examining the distribution of defects in epitaxial layers grown upon silicon wafers, comprising heating at 1200 °C in dry oxygen for 1 to 7 hours. The thermal treatment is followed by removal of the oxide and the growth of an epitaxial layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1 is a graph showing the effect of the temperature of heat treatment on the density of scale-like patterns.

Fig. 2 is a graph showing the effect of the time of heat treatment on the density of scale-like patterns.

Fig. 3 is a graph showing the effect of preheat treatment on the ratio of acceptable products of sufficiently high oxide film dielectric breakdown voltage.

Fig. 4 is a graph showing the relation between the density of scale-like patterns and the speed of crystal growth.

Fig. 5 is a graph showing the relation between the density of scale-like patterns and the ratio of acceptable products of sufficiently high oxide film dielectric breakdown voltage.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In this invention, the heat treatment is given to a wafer which has been cut off a Si single crystal grown grown by the Czochralski method at a speed of pull of not less than 0.8 mm/min. This invention, therefore, has a great significance in allowing production of a Si wafer excellent in oxide film dielectric breakdown voltage characteristic from a Si single crystal grown at the lowest costwise acceptable speed of not less than 0.8 mm/min. by heat-treating the wafer from the single crystal thereby obtaining elimination of crystal defects from the wafer.

Now, this invention will be described below with reference to the accompanying drawings.

Fig. 1 shows the relation between the density of crystal defects (scale-like patterns observable by the selective etching method) and the temperature of heat treatment. It is clearly noted from the diagram that while a Si wafer having a small density of scale-like patterns before the heat treatment has a small density even after the heat treatment, a Si wafer having a large density of scale-like patterns before the heat treatment acquires an effective decrease of the density in consequence of the heat treatment performed at a temperature of not lower than 1,150 °C . Fig. 2 shows the relation between the density of scale-like patterns and the time of the heat treatment at a temperature of 1,200 °C . From this diagram, it is clearly noted that even a Si wafer having a large density of scale-like patterns before the heat treatment acquires an effective decrease in the density of scale-like patterns in consequence of the heat treatment performed for a period of not less than 10 minutes.

In the light of the data described above, the temperature of the heat treatment must exceed 1,150 °C. Further since the upper limit of the working temperature of a quartz tube to be used for the heat treatment is 1,280 °C and since the degree of contamination increases in proportion as the temperature increases, the temperature of the heat treatment contemplated by this invention is limited to the range of from 1,150 °C to 1,280 °C, preferably from 1,150 °C to 1,200 °C. The time of the heat treatment is desired to be not less than 10 minutes, preferably to be in the range of from 10 to 120 minutes. No sufficient elimination of crystal defects is obtained if the time of the heat treatment is less than 10 minutes. The heat treatment tends to impair the economy thereof if

this time exceeds 120 minutes.

<Example>

Now, this invention will be described below with reference to a working example.

Example 1

Several silicon semiconductor single crystal bars 130 mm in diameter were grown by the Czochralski method with the speed of pull varied between 0.4 mm/min. and 1.6 mm/min. These single crystal bars were invariably pulled in the orientation of <100>. Wafers of a prescribed thickness were cut out of each of the single crystal bar with a diamond saw. The wafers were finished as polished wafers by having their surfaces chemically polished.

The Si wafers thus obtained were subjected to the heat treatment and then etched for 30 minutes by the selective etching method to determine the relation between the temperature of the heat treatment and the density of scale-like patterns formed on the etched surfaces. The results are shown in Fig. 1. It is clearly noted from the diagram that even a wafer having a large density of scale-like patterns (abounding in crystal defects) were deprived of the scale-like patterns by the heat treatment at a temperature exceeding 1,150°C , indicating that the heat treatment brought about elimination of crystal defects.

Then, a wafer sample having a density of scale-like patterns of 2,000/cm^2 was heat-treated at a temperature of 1,200°C , to determine the relation between the time of the heat treatment and the density of scale-like patterns. The results are shown in Fig. 2. It is clearly noted from the diagram that the heat treatment at 1,200 °C produced a notable decrease of crystal defects when the time of this heat treatment exceeded 10 minutes.

Subsequently, the heat-treated Si wafer was tested to determine the effect of the heat treatment upon the improvement of oxide film dielectric breakdown voltage characteristic in terms of the relation between the speed of crystal growth and the ratio of conforming products of satisfactorily high oxide film dielectric breakdown voltage. The determination of the oxide film dielectric breakdown voltage characteristic was carried out by forming 100 elements in a given Si wafer and selecting as conforming products the elements whose oxide films exhibited dielectric breakdown voltage exceeding 8 MV/cm. For testing the oxide film dielectric breakdown voltage characteristic, gate parts measuring 8 mm^2 in area and made of polysilicon were used. The formation of an oxide film were carried out at 400°C for 100 minutes (in an atmosphere of dry oxygen). The oxide films had a thickness of 250Å . The results are shown in Fig. 3. In the diagram, the circular mark (O) demotes a sample not undergone the heat treatment, the triangle mark (Δ) a sample preheat-treated at 1,100 °C for two hours (in an atmosphere of dry oxygen), and the square mark (□) a sample preheat-treated at 1,200 °C for two hours (in an atmosphere of dry oxygen). For a fixed speed of crystal growth about of 1.2 mm/min., the ratio of conforming products with sufficiently high oxide film dielectric breakdown voltage from the samples given no heat treatment was about 40%. In the case of the samples subjected to the preheat treatment at 1,100 °C , the ratio of acceptable products was 50%, indicating an improvement of about 10% in the characteristic. In the case of the samples subjected to the preheat treatment at 1,200°C , the rate of acceptable products was 70%, indicating an improvement of about 200% relative to the ratio obtained of the samples given no preheat treatment. The samples given no preheat treatment and excelling in dielectric breakdown voltage characteristic gave a high rate of acceptable products of sufficiently high oxide film dielectric breakdown voltage without reference to the heat treatment, indicating that the Si wafers of this nature retained highly satisfactory oxide film dielectric breakdown voltage characteristic even after a preheat treatment at a high temperature. It is now evident that in Si wafers produced at speeds of crystal growth falling in a wide range, the heat treatment of this invention adapted to the qualities of the Si wafers is effective in improving and uniformization of the oxide film dielectric breakdown voltage characteristics of the Si wafers.

It is clear from the description given above that even from Si single crystals grown at a commercially efficient high speed of crystal growth, the heat treatment of this invention applied as properly adapted allows production of Si wafers excelling in oxide film dielectric breakdown voltage characteristic due to elimination of crystal defects. Consequently, this invention ensures production of LSI in a high yield.

Claims

1. A method for heat treatment of a wafer cut out of a Si single crystal bar grown by the Czochralski method at a speed of pull exceeding 0.8 mm/min. and not higher than 1.6 mm/min. at a temperature in the range 1150°C to 1280°C for the purpose of obtaining a Si single crystal wafer with an improved oxide film dielectric breakdown voltage; characterised by:

   determining, in advance, a first correlation between the oxide film breakdown voltage and the density of scale-like patterns as obtained by selective etching of the wafer, and a second correlation between said density of scale-like patterns and the time period of the heat treatment; and

   heat treating the Si single crystal wafer within said temperature range in an atmosphere of dry oxygen for a time period of at least 10 minutes, selected on the basis of said first and second

correlations such that the Si single crystal wafer has a density of scale-like patterns not higher than 200 counts/cm^2 after the heat treatment, which is required to improve the oxide film dielectric breakdown voltage to not less than 8MV/cm.

2. The method for heat treatment as claimed in Claim 1, wherein the time period of the heat treatment is selected on the basis of said correlation such that a wafer having a density of scale-like patterns between 500 counts/cm^2 and 3000 counts/cm^2 in advance of the heat treatment has said density of scale-like patterns no higher than 200 counts/cm^2 after the heat treatment.

Patentansprüche

1. Verfahren zur Wärmebehandlung eines Wafers, das aus einem Si Einkristallstab herausgeschnitten wurde, der durch das Czochralski-Verfahren mit einer Ziehgeschwindigkeit von mehr als 0.8 mm/min und nicht höher als 1.6 mm/min bei einer Temperatur in dem Bereich von 1150°C bis 1280°C für den Zweck der Bereitstellung eines Si Einkristallwafers mit einer verbesserten dielektrischen Überschlagspannung des Oxidfilms gewachsen wurde; gekennzeichnet durch

   eine vorhergehende Bestimmung einer ersten Wechselbeziehung zwischen der Überschlagspannung des Oxidfilms und der Dichte von skalenähnlichen Mustern, die durch ein selektives Ätzen des Wafers erhalten werden, und einer zweiten Wechselbeziehung zwischen der Dichte der skalenähnlichen Muster und der Zeitdauer der Wärmebehandlung; und

   eine Wärmebehandlung des Si Einkristallwafers innerhalb des Temperaturbereichs in einer Atmosphäre von trockenem Sauerstoff über ein Zeitdauer von wenigstens 10 min, derart ausgewählt auf der Basis der ersten und zweiten Wechselbeziehungen, daß das Si Einkristallwafer eine Dichte der skalenähnlichen Muster von nicht höher als 200 Zählungen/cm^2 nach der Wärmebehandlung hat, was erforderlich ist, um die dielektrische Überschlagspannung des Oxidfilms auf nicht weniger als 8 MV/cm zu verbessern.

2. Verfahren zur Wärmebehandlung nach Anspruch 1, bei welchem die Zeitdauer der Wärmebehandlung derart auf der Basis der Wechselbeziehung gewählt wird, daß ein Wafer mit einer Dichte der skalenähnlichen Muster zwischen 500 Zählungen/cm^2 und 3.000 Zählungen/cm^2 vor der Wärmebehandlung diese Dichte der skalenähnlichen Muster von nicht höher als 200 Zählungen/cm^2 nach der Wärmebehandlung hat.

Revendications

1. Méthode de traitement thermique d'une galette découpée dans un barreau de Si monocristallin obtenu par tirage selon le procédé Czochralski à une vitesse de tirage supérieure à 0,8 mm/min mais ne dépassant pas 1,6 mm/min, à une température comprise entre 1150 et 1280°C, afin d'obtenir une galette de Si monocristallin ayant une meilleure tension diélectrique de claquage du film d'oxyde, caractérisée en ce qu'elle comprend :

   la détermination préalable d'une première corrélation entre la tension diélectrique de claquage du film d'oxyde et la densité des motifs en écailles obtenus par une attaque chimique sélective de la galette et d'une seconde corrélation entre ladite densité des motifs en écailles et la durée du traitement thermique ; et

   le traitement thermique de la galette de Si monocristallin dans ladite plage de température sous atmosphère d'oxygène sec pendant une durée d'au moins 10 minutes, choisie en fonction des première et seconde corrélations, de telle sorte que la galette de Si monocristallin ait une densité de motifs en écailles qui ne dépasse pas 200 unités / cm^2 après traitement thermique, densité requise pour améliorer la tension diélectrique de claquage du film d'oxyde jusqu'à une valeur d'au moins 8 MV/cm.

2. Méthode de traitement thermique selon la revendication 1, dans laquelle la durée du traitement thermique est choisie en fonction desdites corrélations de telle sorte que, pour une galette ayant une densité de motifs en écailles comprise entre 500 unités / cm^2 et 3 000 unités / cm^2 avant traitement thermique, ladite densité de motifs en écailles ne soit pas supérieure à 200 unités / cm^2 après traitement thermique.

FIG. 1

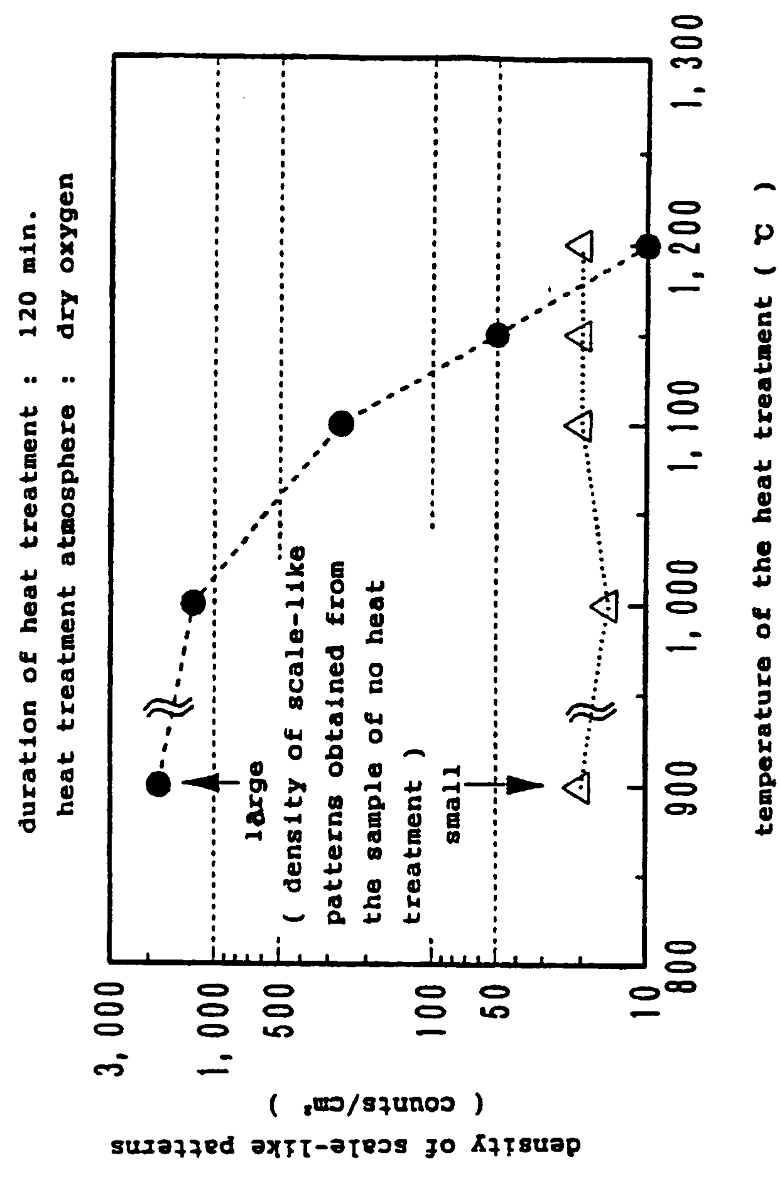
duration of heat treatment : 120 min.
heat treatment atmosphere : dry oxygen
large
(density of scale-like patterns obtained from the sample of no heat treatment)
small
temperature of the heat treatment (℃)
800
900
1,000
1,100
1,200
1,300
3,000
1,000
500
100
50
10
density of scale-like patterns
(counts/cm²)

FIG. 2

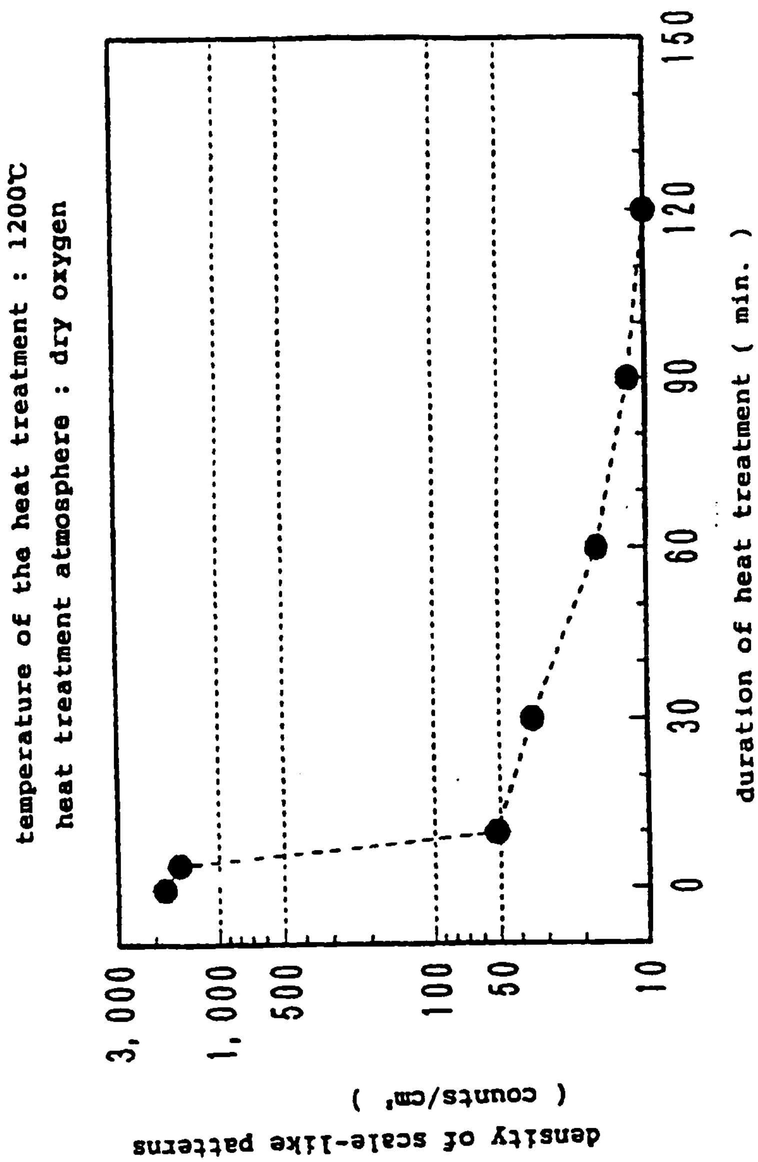
temperature of the heat treatment : 1200℃
heat treatment atmosphere : dry oxygen
duration of heat treatment (min.)
0
30
60
90
120
150
density of scale-like patterns
(counts/cm²)
3,000
1,000
500
100
50
10

FIG. 3

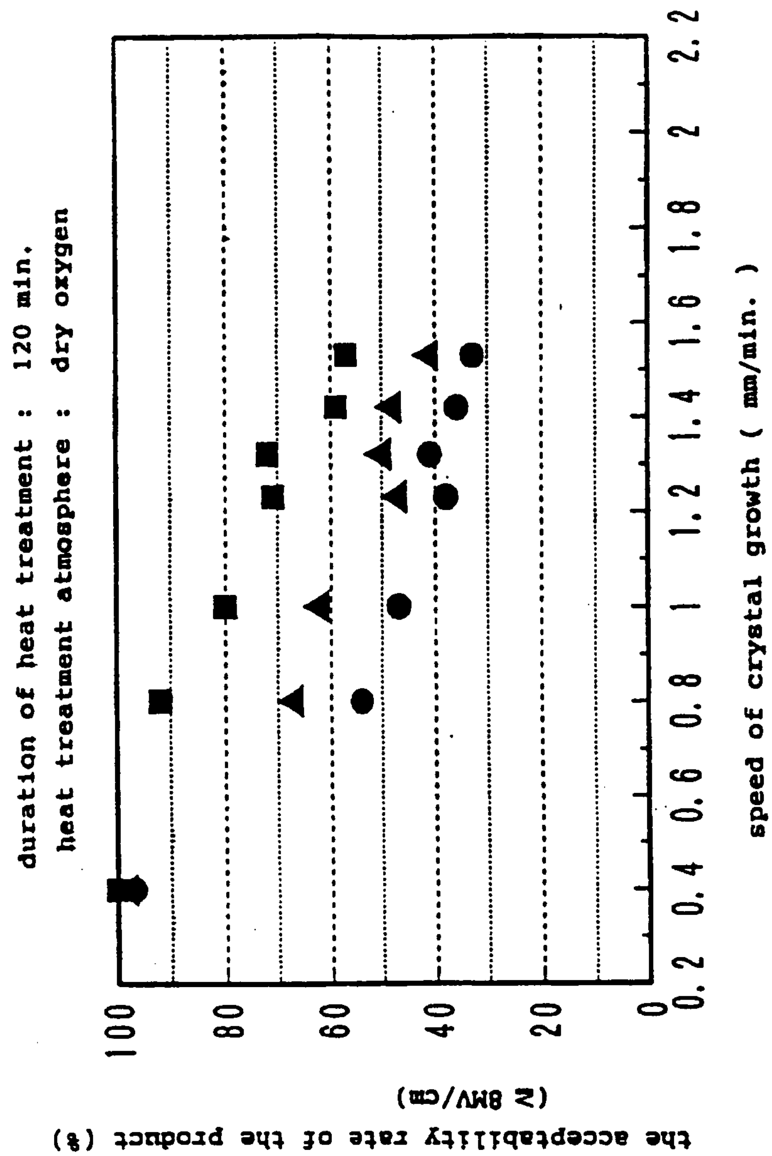
duration of heat treatment : 120 min.
heat treatment atmosphere : dry oxygen
speed of crystal growth (mm/min.)
0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2 2.2
the acceptability rate of the product (%)
(≧ 8MV/cm)
0 20 40 60 80 100

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FIG.4

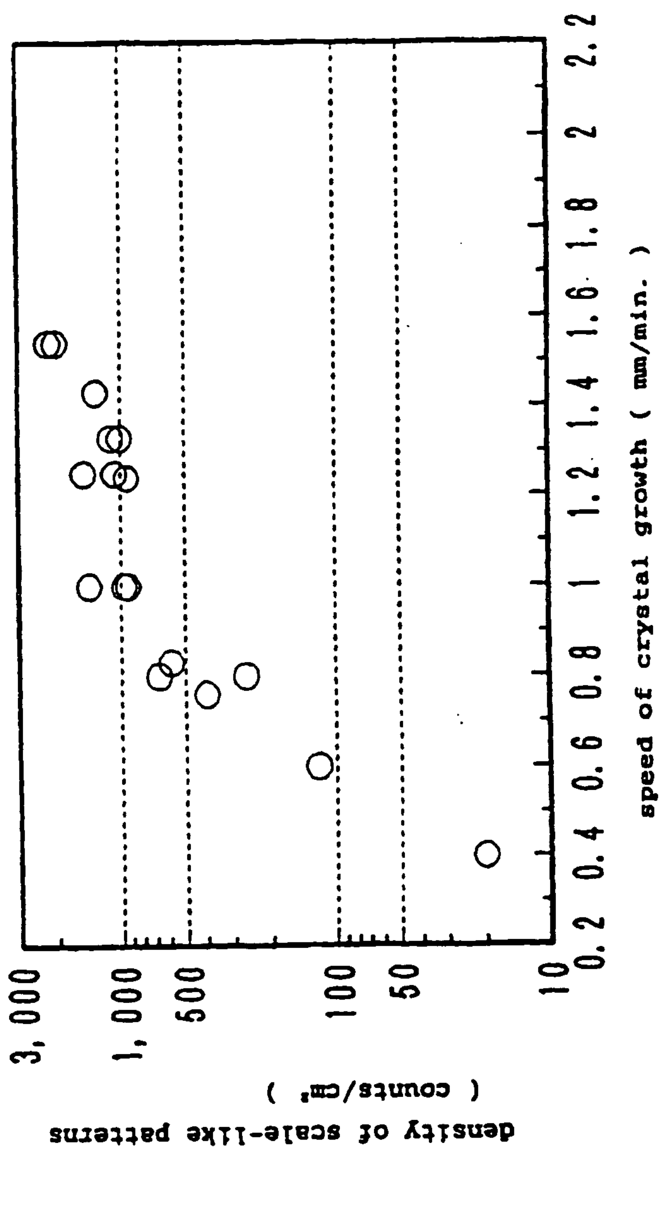
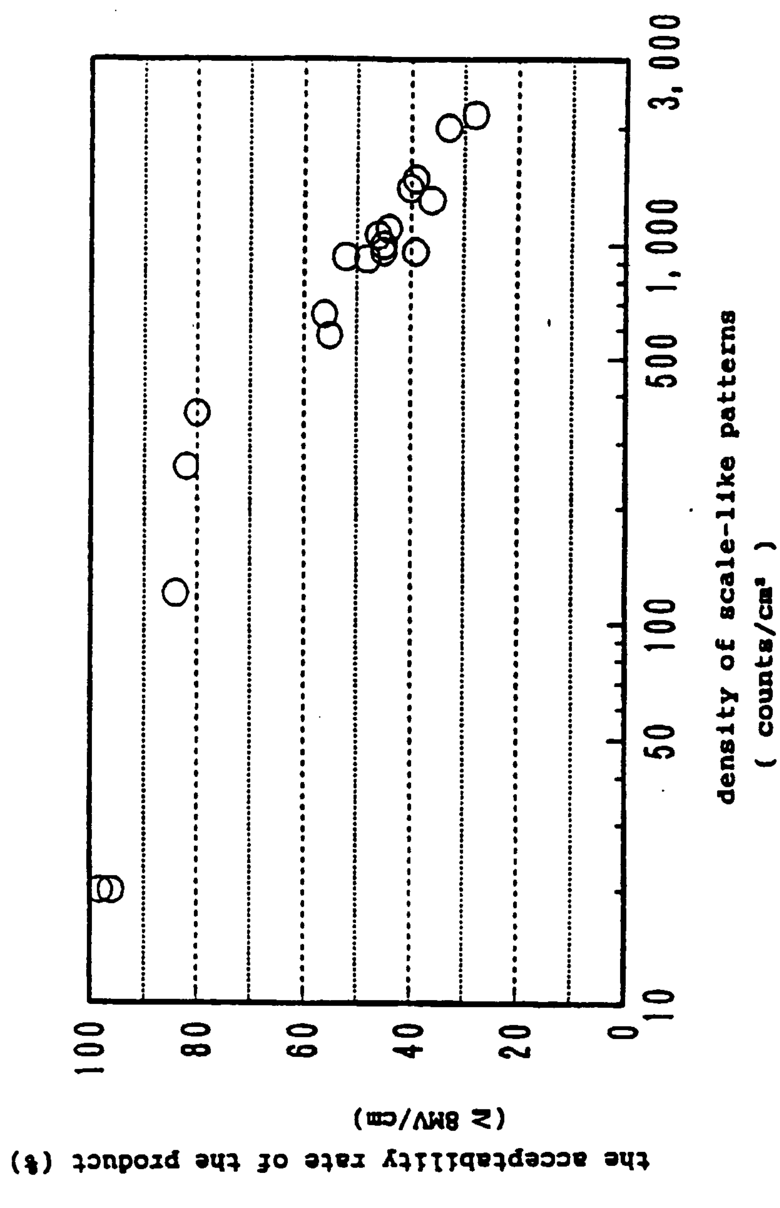


FIG. 5


density of scale-like patterns
(counts/cm²)
10
50
100
500
1,000
3,000
the acceptability rate of the product (%)
(≧ 8MV/cm)
0
20
40
60
80
100